

III.B.4 Diesel Reforming for Solid Oxide Fuel Cell Auxiliary Power Units

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Objectives

- Research and develop technologies for cost-effective and durable onboard diesel reformers for solid oxide fuel cell (SOFC) auxiliary power unit (APU) applications
- Examine fundamentals of the diesel reforming process
 - Characterize the key parameters of the diesel reforming process
 - Fuel vaporization, mixing and reactor feed conditions
 - SOFC anode exhaust recycle for water availability
 - Determine the factors that limit durability
 - Catalyst sintering and deactivation
 - Carbon formation during operation and startup
 - Develop and test processes to extend durability
- Develop models to provide a design and operation basis for diesel reforming
 - Modeling of carbon formation
 - Modeling of SOFC anode exhaust recycle system
 - Kinetic modeling to describe details of diesel reforming process

Approach

- Examine catalytic partial oxidation and steam reforming
 - Experimental measurements
 - Isothermal reforming measurements for detailed kinetic measurements
 - Adiabatic reformer operation for development of SOFC anode recycle simulation and appropriate fuel feed conditions
 - Modeling
 - Carbon formation equilibrium
 - Reformer operation with anode recycle

Accomplishments

- Conducted experimental measurements of diesel reforming
 - Simulated real-world diesel reforming operation
 - Evaluated the effect of SOFC anode exhaust recycle on reactor operation
 - Defined the effect of sulfur containing hydrocarbons on carbon formation

- Defined the effect of aromaticity levels on carbon formation
- Examined catalyst sintering
- Examined reforming activity and carbon formation tendency of nano-particle nickel catalysts
- Conducted modeling of carbon formation and diesel reforming with recycle operation
 - Modeled reformer efficiency and parasitic losses due to the effects of anode exhaust recycle
 - Defined different thermodynamic states of carbon

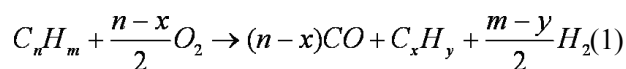
Future Directions

- Examine reformer durability
 - Catalyst sintering and deactivation
 - Stabilize active catalyst particles
 - Reformer operational profiles for reducing catalyst sintering
 - Examine multipoint air injection to reduce oxidation temperature
- Study carbon formation
 - Examine additives (such as dimethyl ether and oxygenates) for tendency to prevent carbon formation
 - Investigate stand-alone startup and processes
- Determine reformer durability and hydrocarbon breakthrough effect on SOFC
 - Incorporate SOFC ‘button’ cell operating on reformat
- Complete carbon formation model and distribute
 - Develop ‘user-friendly’ interface and user manual

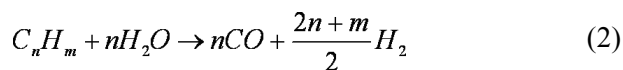
Introduction

The use of a solid oxide fuel cell (SOFC) to provide auxiliary power for diesel trucks can increase fuel efficiency and reduce emissions by reducing diesel engine idling time. The potential high-volume market for SOFC auxiliary power units (APUs) could provide the driver for high-volume manufacturing to reduce the cost of SOFC modules, a key goal of the Solid State Energy Conversion Alliance (SECA) program. The logical fuel of choice for a diesel truck SOFC APU is diesel fuel. SOFCs are being researched that directly oxidize hydrocarbon fuels, but the power densities are lower than those of SOFCs that use the products of reforming diesel fuel – H₂, CO, CO₂, H₂O, N₂, and hydrocarbons such as methane. Since the SOFC is the most costly component of the system, increasing the power density provides benefits in reducing volume, mass, and cost that can offset the cost and complexity of adding a diesel reformer to the system. The objective of this project is to research and develop the technology to enable that diesel reformer to be cost-effective and durable.

Diesel fuel can be reformed into a H₂/CO-rich fuel feed stream for an SOFC by autothermal reforming (ATR), a combination of partial oxidation (POx),



and steam reforming.



The typical autothermal reformer is an adiabatic, heterogeneous catalytic reactor, and the challenges in its design and operation, particularly durable operation, on diesel fuel are manifold. These challenges begin with the vaporization and mixing of diesel fuel with air and steam where pyrolysis can occur and improper mixing leads to hot spots and incomplete conversion. Carbon formation during operation and startup can lead to catalyst deactivation and fouling of downstream components, reducing durability. The exotherm of the POx reaction can generate temperatures in excess of 800°C [1], where catalysts rapidly sinter, reducing their lifetime.

Water addition helps to reduce carbon formation, so a key issue becomes the source of the water onboard the vehicle. Our research begins to address these issues through an experimental and modeling examination of the fundamentals of these processes. The intent is to provide a design and operation basis for a durable diesel reformer for an SOFC APU.

Approach

Our approach employs experimental measurements in diesel reformer reactors and microscale reactors along with development and application of chemical models to interpret and codify experimental results. Experimental measurements of diesel reforming are made in an adiabatic heterogeneous catalytic reactor to simulate real-world diesel reformer operation and to identify commercial design issues. Experiments conducted in the adiabatic reactor were complemented by experiments conducted in a well-controlled and well-defined isothermal microscale reactor, which can be used for measurements of kinetics of diesel reforming.

The equilibrium conditions for carbon formation have been modeled as a function of operating conditions, fuel composition, and thermodynamics of deposited carbon species. Modeling of the reformer system and SOFC anode recycle was conducted to examine the relative parasitic losses due to recycling the SOFC anode.

Modeling Results

The equilibrium composition in a chemically reacting system is a function of the final temperature, pressure and the feed composition. The conditions for forming solid carbon were determined from the equilibrium compositions of reactions at various temperatures, pressures and feed compositions. Modeling of the equilibrium conditions for the formation of solid carbon has led to the conclusion that the thermodynamics of the actual carbon are poorly understood. As a result, we have modeled the thermodynamics of carbon formation.

Two forms of amorphous carbon come from the two following reactions:

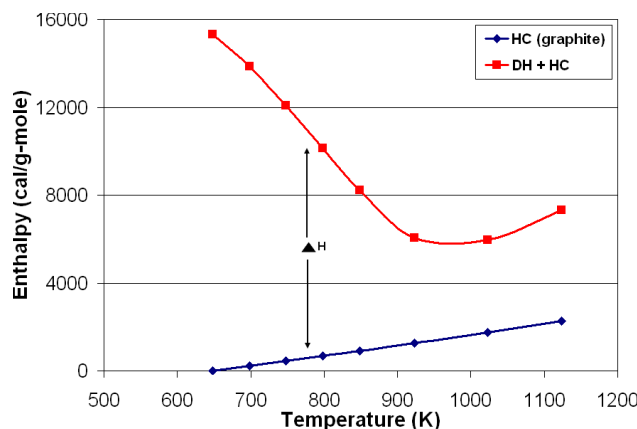


Figure 1. Enthalpy for C_2^* Carbon, Referenced to Graphite, with 0 Enthalpy at 648 K



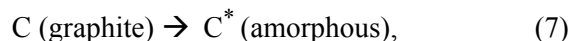
A heat capacity for graphite carbon [2] is:

$$C_p = 4.03 + 0.00114T - 204000/T^2 \quad (5)$$

For a constant temperature reaction,

$$G = H - TS \quad (6)$$

For the reaction



graphite converting to any amorphous carbon, G becomes G_f , the Gibb's free energy of formation for the amorphous carbon. Since

$$dH = C_p dT, \text{ then } H = H_{\text{ref}} + \int C_p dT, \quad (8)$$

we can then integrate from reference 298 K to some desired temperature T . Figure 1 is a plot showing computed H for graphite and amorphous carbon. H was computed by means of adding the change in Gibb's Function with respect to T to the graphite numbers in each case to give the upper curves.

The important conclusion from Figure 1 is that the upper curves show a negative heat capacity for the amorphous carbons in general. Since $H_1 - H_2 = C_p (\text{average})(T_1 - T_2)$, the upper curves in all the figures, for at least the lower temperature range, show that $C_p (\text{average})$ has to be negative. These calculations verify that our data do predict negative heat capacities (impossible) over at least some temperature ranges. We should also note that

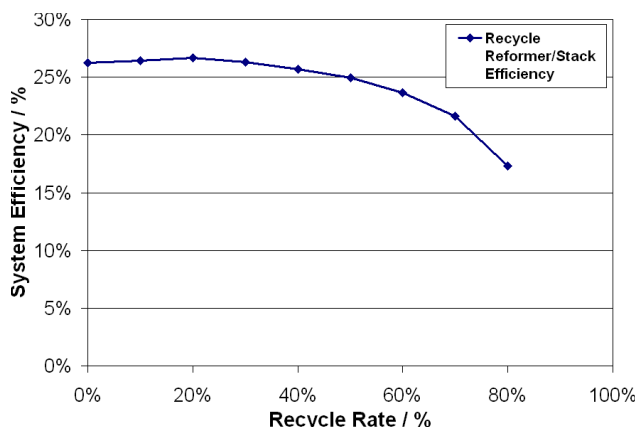


Figure 2. Effect of Anode Recycle on System Efficiency from Compression Energy Penalty

some of the data, at higher temperatures, do predict positive heat capacities. These carbon enthalpies show that carbon thermodynamics are not consistent over a range of temperatures. Apparently, carbon species with different thermodynamics are formed; something like a phase change or a change in carbon composition is happening to these amorphous carbons over the range of temperatures.

To supply water for the reforming reaction, the anode gas of the SOFC can be recycled to the reformer. This requires compression and, thus, a parasitic loss to the system. To compare relative performance measures as a function of recycle ratio, this was modeled. To accomplish the efficiency modeling, a number of assumptions were used, including constant SOFC fuel utilization of 0.5, constant SOFC operating voltage of 0.7 V and good thermal integration of the SOFC anode gas recycle with the diesel reformer. A minimum outlet reformer temperature of $\sim 800^{\circ}\text{C}$ was used. The results of this modeling are summarized in Figure 2.

At the lowest recycle ratios, there is not enough water available to conduct the reforming reaction; therefore, the efficiency is lower as high oxygen/carbon ratios must be used to convert the hydrocarbons to H_2 and CO. As the recycle ratio increases, the parasitic power consumption increases; however, the oxygen requirement decreases due to recycled water. It appears that the maximum efficiency is obtained at approximately 20% recycle ratio.

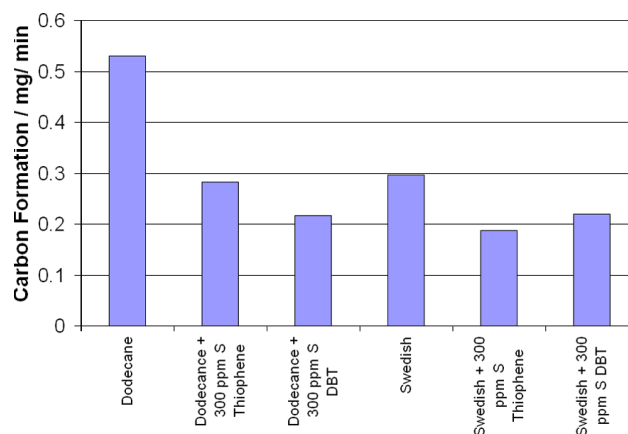


Figure 3. Sulfur-Containing Hydrocarbon Compound Effect on Carbon Formation; Addition of Thiophene and Dibenzothiophene to Dodecane and Low-Sulfur Swedish Diesel Fuel at 300 ppm S

Experimental Results

The design and operation of the diesel reformer with recycle operation has been previously reported [3], as has the carbon formation for a number of operating conditions [4]. In prior experiments, commercial diesel fuel showed a higher propensity for carbon formation than did low-sulfur Swedish diesel fuel, and one hypothesis was that this was due to the sulfur content. Carbon formation with the commercial diesel fuel was on average three times higher than that for the low-S Swedish diesel fuel.

Experiments were conducted using an isothermal microscale reactor to clarify the effects of sulfur and the aromatic content of the hydrocarbons. Figure 3 shows carbon formation for low-sulfur Swedish diesel fuel and dodecane ($\text{C}_{12}\text{H}_{24}$) with and without 300 ppm sulfur added as thiophene and dibenzothiophene (DBT) for autothermal reforming (ATR) ($\text{O/C} = 1.0$, $\text{S/C} = 0.34$). The ATR conditions simulate similar adiabatic measurements for an SOFC anode recycle of 35%. The addition of sulfur compounds (thiophene and DBT) does not increase carbon formation, although higher carbon formation was observed from pure dodecane than from Swedish diesel. There was also no detectable sulfur (by x-ray fluorescence) in carbon samples regardless of sulfur content in fuel (dodecane and low-S Swedish diesel fuel). The carbon formation mechanism does not

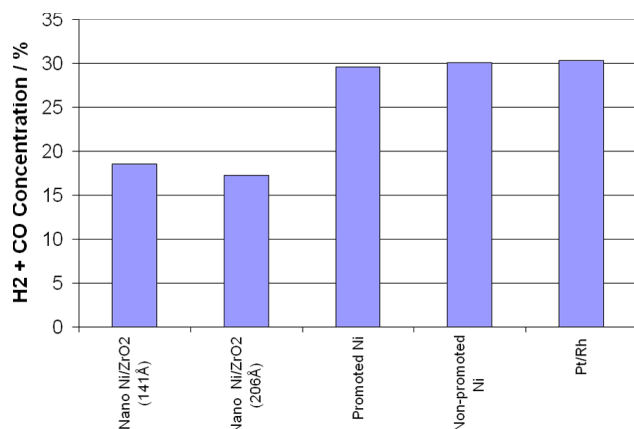


Figure 4. Hydrogen plus CO Concentrations for Nano-Particle Nickel Supported on Zirconia, Nano-Particle Nickel, Promoted Nickel, Non-Promoted Nickel and Pt/Rh

seem be affected by the presence of sulfur or these sulfur compounds.

Carbon formation measurements were also made with the addition of various aromatic and cyclic components, specifically, xylene, decalin, tetralin, naphthalene, anthracene and phenanthrene. When these compounds were added to low-sulfur Swedish diesel fuel, the carbon formation (during ATR at constant O/C = 0.95) was increased nearly uniformly by a factor of 2x. When these components were added to dodecane, increased carbon formation was observed with the 2- and 3-ringed aromatic components (naphthalene, anthracene and phenanthrene).

Carbon formation shows different tendencies with different catalysts and tends to be worse over nickel catalysts. However, results have shown that nano particle nickel catalysts can show higher stability than traditional nickel catalysts during the steam reforming of CH₄. Thus, these catalysts were examined for their capability for reforming of diesel fuel. Figure 4 shows the outlet concentrations of hydrogen plus carbon monoxide during diesel reforming over various nickel catalysts and a standard Pt/Rh reforming catalyst. Good activity for the nanocomposite nickel catalysts was not observed, as the diesel fuel conversion was not complete; in addition, a higher propensity for carbon formation was observed with nanocomposite nickel catalysts. Potentially, these nanoparticle nickel catalysts have a

better application as SOFC anodes for CH₄ conversion.

Conclusions

- Diesel fuel reforming has been conducted under isothermal and adiabatic conditions.
- Diesel reforming under adiabatic operation was performed with simulated SOFC anode recycle.
- Modeling suggests that the optimum efficiency point for diesel reforming occurs with SOFC anode recycle of ~20% due to required O/C, reformer temperature and parasitic compression losses.
- Carbon formation mechanism does not seem to be affected by the presence of sulfur or the presence of sulfur compounds (thiophene and dibenzothiophene).
- Addition of cyclic and multi-ringed aromatic components increases carbon formation.
- Modeling shows that carbon thermodynamics are not constant with temperature.
- Different thermodynamic carbon species appear to be formed.
- Nanoparticle nickel catalysts do not appear suitable for diesel reforming.

FY 2005 Publications/Presentations

1. DIESEL REFORMING FOR SOFC AUXILIARY POWER UNITS, Rodney L. Borup, Michael A. Inbody, José I. Tafoya, Dennis R. Guidry and W.J. Parkinson, Fuel Cell Seminar, San Antonio, Texas, November 1-5, 2004.
2. EFFECT OF SOFC ANODE EXHAUST RECYCLE ON DIESEL REFORMING, Rodney L. Borup, Michael A. Inbody, W.J. Parkinson, Dennis R. Guidry and Eric L. Brosha, 5th Annual Logistic Fuel Processing Conference, Panama City, Florida, January 25-26, 2005.
3. EFFECT OF SOFC ANODE EXHAUST RECYCLE ON DIESEL REFORMING, Rodney L. Borup, Michael A. Inbody, W.J. Parkinson, Dennis R. Guidry and Eric L. Brosha, 2nd International Symposium on Solid Oxide Fuel Cells, Cocoa Beach, Florida, January 23-28, 2005.
5. DIESEL REFORMING FOR AUXILIARY POWER UNITS, Rodney L. Borup, Michael A. Inbody, W.J. Parkinson, Dennis R. Guidry and Eric L. Brosha,

- DOE SECA CTP (Solid State Energy Conversion Alliance Core Technology Program), Tampa Bay, Florida, January 27, 2005.
6. DIESEL REFORMING WITH SOFC ANODE RECYCLE, Rodney L. Borup, Michael A. Inbody, W.J. Parkinson, and Dennis R. Guidry, ECS - Electrochemical Society, Las Vegas, NV, June 12-17, 2005.
 7. DIESEL REFORMING WITH SOFC ANODE EXHAUST RECYCLE, Rodney L. Borup, Michael A. Inbody, W.J. Parkinson, Dennis R. Guidry and Eric L. Brosha, Fuel Cell Seminar, Palm Springs, CA, To be presented November 14-18, 2005.

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1. Ahmed, S., Presentation to Department of Energy, Washington DC, May 01, 2003.
2. Stull, D.R. and Prophet, H., eds. JANAF Thermochemical Tables, 2nd. Ed., U.S. Dept of Comm., U.S. Gov. Prtg Off. Washington, D.C. 1971.
3. Borup, R.L., Parkinson, W.J., Inbody, M.A., Tafoya, J.I. and Vigil, W.J., "*Diesel Reforming for SOFC APU*", DOE SECA Program, FY 2003 Progress Report (2003).
4. Borup, R.L., Parkinson, W.J., Inbody, M.A., Tafoya, J.I. and Guidry, D.R., "*Diesel Reforming for Solid-Oxide Fuel Cell Auxiliary Power Units*", DOE SECA Program, FY 2004 Progress Report (2004).